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One-Electron Photooxidation of Porphyrins at Low Temperature

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The π-cation radicals of the metalloporphyrins magnesium octaethylporphyrin (MgOEP), magnesium tetraphenylporphyrin (MgTPP), and zinc tetraphenylporphyrin (ZnTPP), as well as the free base porphyrins of tetratolylporphyrin (H_2TTP) and tetraphenylporphyrin (H_2TPP) have been formed at liquid nitrogen temperatures in a rigid matrix of alkyl chloride glasses containing CCl_4 or 1,1,2,2-tetrachloroethane (TCE), following photolysis of the porphyrins with visible light. The reaction proceeds via *electron transfer from the photoexcited porphyrin to the solvent molecules; the efficiency of this electron transfer may be qualitatively evaluated in terms of electron tunneling in the solid matrices. This is the first report of the photochemical formation of a free base porphyrin π-cation radical species.*

Introduction

Porphyrin π-cation radical species are known to play an important role in both biological and photochemical reactions. Oxidized porphyrins are involved in the reactions of catalase and peroxidase enzymes [1, 2], as well as the photosynthetic pathway involving chlorophyll-based reaction centres [3, 4]. Although oxidized porphyrins have been produced chemically [5], photochemical synthesis of porphyrin π-cation radical species [6] offers a potentially efficient route to synthetic chlorophyll-like photochemical systems [7]. In liquid solutions, one-electron photooxidation of porphyrins can involve the porphyrin low energy excited states which may transfer electrons to many different types of acceptor molecules following collision in solution [6, 8–12]. However, the collision mechanism of electron transfer is not appropriate for reactions in rigid matrices, such as glassed solvents at low temperature, or protein- and membrane-bound hemes and chlorophylls. In a rigid matrix, it is generally accepted that electron transfer will occur by tunnelling, because the reactants are held apart at fixed distances, although the minimum separation of the donor and acceptor molecules which is required to prevent electron transfer is not known.

In recent measurements of phosphorescence and fluorescence quenching in rigid media by long range electron transfer from the excited states of aromatic molecules [13, 14] and ruthenium complexes [15] to acceptor molecules, the lack of a measurable accumulation of electron transfer products was thought to be due to an efficient back reaction which prevented the charge separation from being maintained. However, if the back reaction is negligible, the stable trapping of the primary electron transfer products in the rigid matrix will allow their characterization by spectroscopic techniques.

The photochemical oxidation of porphyrins to the cation radical species has been found to occur in frozen solutions when donor–acceptor complexes of porphyrins and certain electron acceptors were irradiated [16–18]. In earlier work [19] it was claimed that the solvent can act as the electron acceptor in the case of a biphotonically ionized porphyrin in frozen solution, and recently, Konishi *et al.* [20, 21] applied the method of positive-hole scavenging in γ-irradiated alkyl chloride glasses to produce porphyrin π-cation radical species.

In the present communication we report photolytic experiments involving the synthetic porphyrins, free base tetratolylporphyrin (H_2TTP) and tetraphenylporphyrin (H_2TPP), MgTPP, ZnTPP and magnesium octaethylporphyrin (MgOEP)[†] each embedded in alkyl chloride glasses. We are able, for

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[†] MTPP, (α,β,γ,δ-tetraphenylporphyrinato)metal(II), and MOEP, (octaethylporphyrinato)metal(II).

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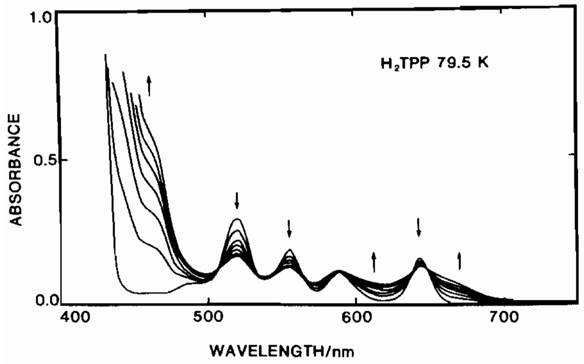

Fig. 1. Absorption spectrum changes during photolysis of tetraphenylporphine in a s-butyl chloride-tetrachloroethane glassy solution (1:1 v/v) at 79.5 K. The spectra were recorded after 0, 1, 2, 3, 4, 5 and 6 min of irradiation.

the first time, to demonstrate that a low energy excited state of these porphyrins, formed by irradiation with visible light in a rigid matrix, can transfer an electron to the solvent yielding the charge separated electron transfer products.

Experimental

H_2TTP, H_2TPP, ZnTPP, and MgTPP were synthesized according to the published procedures [22]. MgOEP was kindly supplied by Dr. J. Fajer, Brookhaven National Laboratory, U.S.A. Reagent grade TCE (Fisher) was purified by treatment with several changes of concentrated sulfuric acid, washed with aqueous sodium hydroxide and water, and finally distilled under nitrogen. Reagent grade sec-butyl chloride, BuCl, (BDH) and Spectranalysed CCl_4 (Fisher) were used without further purification. Each porphyrin sample was dissolved in an alkyl chloride solvent, the solution was placed in an optical cell which had a path length of about 0.1 cm, which was then plunged into liquid nitrogen in order to glass the solution. This glass was then quickly transferred into an Oxford Instruments (UK) CF204 flow cryostat. The optical absorption spectrum of each sample in the CF204 cryostat was recorded on a Cary 17 spectrophotometer; the temperature was controlled by means of a CLTS probe mounted on the cryostat and an Oxford Instruments DTC2 temperature controller. The absorption spectra were automatically digitized, and the baselines which were recorded for the neat solvents were subtracted by computer from the data of the sample. A 300 W tungsten-halogen visible light projector lamp, controlled by a variable transformer, was used for the photolysis of the samples.

EPR spectra of the porphyrin samples which were glassed in liquid nitrogen, were recorded at about 100 K, on a Varian E12 X band 100 kHz spectrometer interfaced with a Nicolet 1180 computer through a Nicolet Explorer III digital oscilloscope. The temperature in the insert dewar of the EPR cavity was controlled by a Varian E-257 temperature controller.

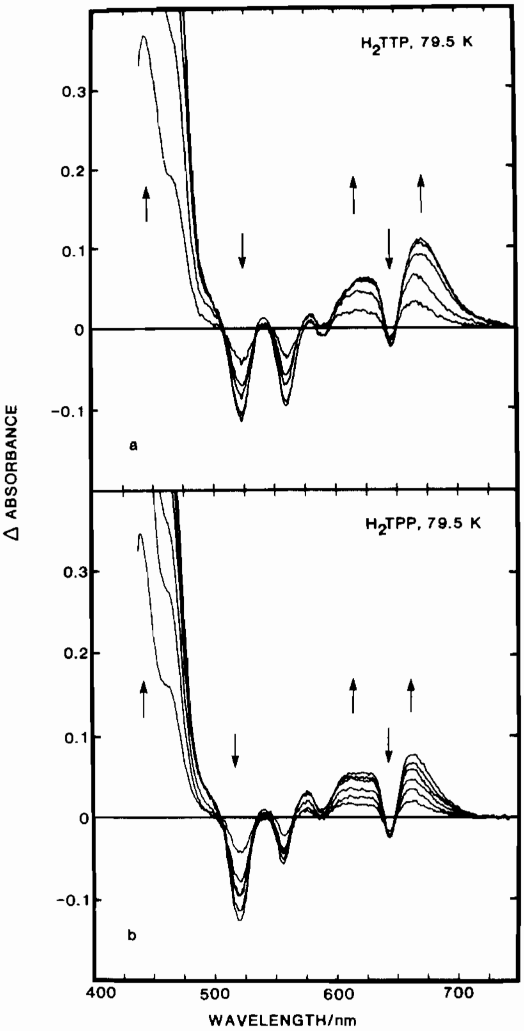

Fig. 2. Absorption difference spectra between the spectra of irradiated and non-irradiated solutions of (a) tetratolyloporphine and (b) tetraphenylporphine in s-butyl chloride-TCE (1:1 v/v) glass at 79.5 K. The irradiation time was 1, 3, 4, 6 and 7 min for H_2TTP, and 1, 2, 3, 4, 5 and 6 min for H_2TPP with the lamp in a fixed arbitrary position relative to the sample cell.

Results

The change in the optical absorption spectrum of H_2TPP in a 1:1 v/v BuCl–TCE glassy solution at 79.5 K following irradiation from the tungsten halogen source is shown in Fig. 1. When the H_2TPP

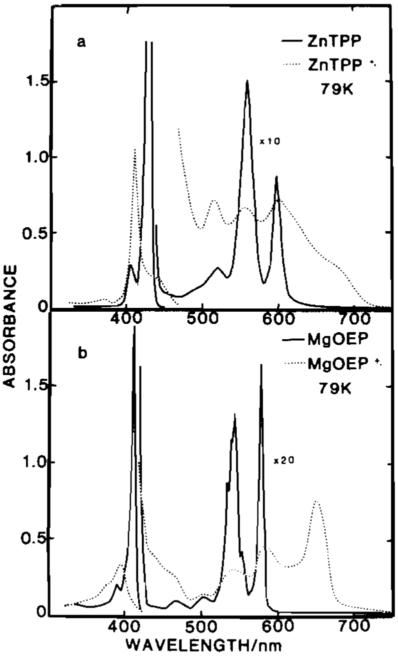

Fig. 3. Optical absorption spectra of (a) ZnTPP and its photochemical product, and (b) MgOEP and its photochemical product in a s-butyl chloride–CCl_4 glassy solution at 79 K. The spectra of the products were obtained after an exhaustive photolysis of the samples.

solution was cooled to 79.5 K the relative intensities of the absorption bands in the visible region changed only slightly, and no new absorption bands were observed in any of the alkyl chloride mixtures, indicating that no charge-transfer complexes between the porphyrin and the solvent molecules had formed. The visible region absorption bands of H_2TPP, located at 647, 592, 548 and 515 nm, decrease on irradiation at 79.5 K, and new absorption bands, at about 675 nm and at 445 nm, begin to appear.

Figure 2 shows the absorption difference spectra calculated from the spectra of irradiated and non-irradiated solutions of (a) H_2TTP and (b) H_2TPP in BuCl–TCE glass at 79.5 K. The changes in the absorption spectra shown in Figs. 1 and 2 can be ascribed to a gradual conversion of H_2TTP and H_2TPP into their corresponding π-cation radical species. To our knowledge, the absorption spectra for one-electron-oxidized free base tetraphenyl- and tetratolylporphines have not been previously reported. The conversion of H_2TPP or H_2TTP to a single oxidized species in the irradiated solutions is supported by the observation of the isosbestic points in Figs. 1 and 2. Support for the assignment of the photochemical product of H_2TPP and H_2TTP as the π-cation radical species can be obtained from

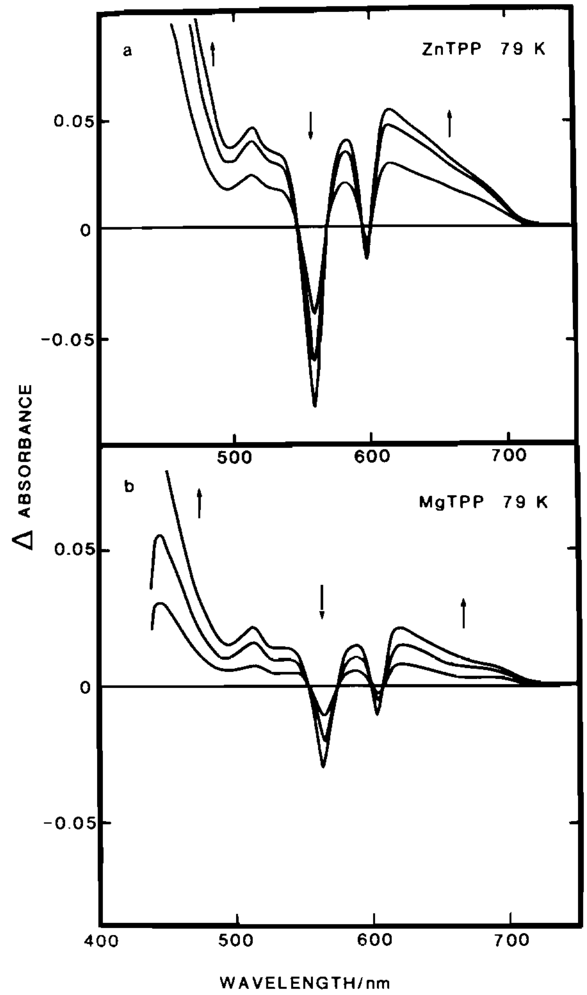

Fig. 4. Absorption difference spectra between the spectra of irradiated and non-irradiated solutions of (a) zinc tetraphenylporphine, and (b) magnesium tetraphenylporphine in s-butyl chloride–CCl_4 (1:1 v/v) glass at 79 K. The irradiation time was 10, 60 and 180 s for ZnTPP and 10, 15 and 120 s for MgTPP.

EPR measurements (see below). A complete conversion is not easily obtained, since the yield or efficiency of the photochemical reaction is very low when compared to the yield of the corresponding reactions of metalloporphyrins (see Table I).

Figure 3 shows the absorption spectra of (a) ZnTPP and its photochemical product, and (b) MgOEP and its photochemical product in a BuCl–CCl_4 glass at 79 K. The spectra of the photolytic products were obtained after exhaustive photolysis of the porphyrin solutions at 79 K using visible light. The products of ZnTPP and MgOEP photolysis in the rigid solutions exhibit optical absorption spectra that are only slightly different from the spectra of the $ZnTPP^{+\cdot}$ and $MgOEP^{+\cdot}$ cation radical

TABLE I. Electron Transfer Yields and Energetics for the Reaction of Photoexcited Porphyrins with TCE in Solid Matrices.

Porphyrin	Rel. Yield[a]	τ_p/ms[b]	E(T)/eV[c]	$E_{1/2}$/V[d]	ΔG(Et)/eV[e]
MgTPP	1.00	45	1.48	0.54	−0.04
ZnTPP	0.37	26	1.59	0.71	0.02
H_2TPP	0.04	6	1.43	0.95	0.42

[a] Relative yield of radical formation for equivalent irradiation at 77 K. [b] Phosphorescence lifetime at 77 K [32]. [c] Triplet excited state energy [32]. [d] Oxidation potential (*vs.* SCE) in methylene chloride solution [33]. [e] Thermodynamic potential change for the electron transfer reaction from electrochemical data in liquid solution, assuming $E_{1/2}$ = −0.9 V for the reaction $C_2H_2Cl_4 + e^- \rightarrow (C_2H_2Cl_3\cdot + Cl^-)$, and the participation of the triplet state.

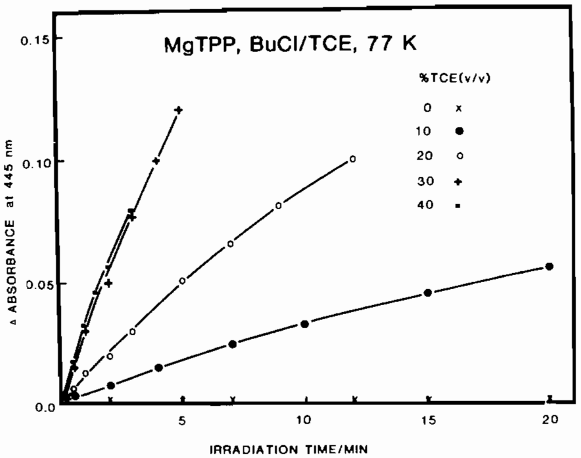

Fig. 5. The dependence of the optical absorption changes associated with the photolysis of MgTPP in s-butyl chloride-TCE glasses at 77 K on the concentration of TCE.

species formed in liquid solution by chemical and electrochemical techniques [5, 23]. Figure 4a, which shows absorption difference spectra calculated from the initial spectrum and spectra recorded during photolysis, demonstrates changes in the optical spectrum of ZnTPP when irradiated in a BuCl–CCl_4 glass at 79 K. Quite similar optical absorption spectrum changes are obtained during the photolysis of MgTPP in the TCE–CCl_4 frozen solution at a somewhat higher quantum efficiency (Fig. 4b). As in the case of H_2TPP photolysis the observation of isosbestic points in these spectra indicates that photochemical conversion to a single oxidized species had occurred.

The change in the absorption spectrum of MgTPP at 445 nm which is a region of low absorption in the unoxidized porphyrin, following photolysis in frozen solutions of BuCl as a function of the content (0% to 40%) (v/v) TCE is shown in Fig. 5. The initial yield of the photolysis product, as indicated by an increase in absorption at 445 nm, strongly depends on the concentration of TCE in the mixed solvent glasses for all the porphyrins studied. The dependence of the yield of the photolysis product, ϕ, on the TCE concentration, c, fails to fit the Stern-Volmer equation,

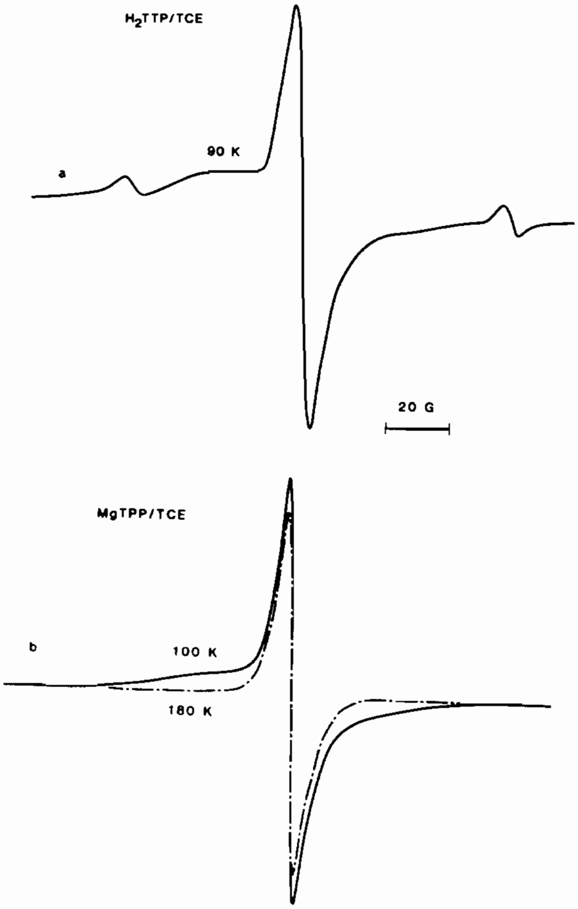

Fig. 6. EPR spectra of irradiated TCE solutions of (a) H_2TTP at 90 K, and (b) MgTPP at 100 K and 180 K. EPR detection conditions: modulation amplitude, 0.32 mT; microwave power, 1 mW, at ~9.0 GHz.

$$1/\phi = (1/b)(1 + 1/Kc),$$

where b and K are constants, thus a simple complexation-quenching mechanism based on the degree of complexation cannot be used to explain the observed concentration effect on the photolysis yield. Table I shows the relative yields of photolytic products of several porphyrins, determined from the absorption change at high concentration of TCE.

The EPR spectra recorded for H_2TPP and MgTPP after photolysis in a TCE-containing glass at about 100 K share the common features of a sharp singlet superimposed on a broad signal, Fig. 6. When the irradiated solution of MgTPP was warmed to 180 K the broad signal decayed, and the sharp signal became the same as the signal reported for $MgTPP^{+\bullet}$ [3]. The EPR spectra recorded for ZnTPP photolysed in the alkyl chloride glasses at low temperatures exhibit similar behaviour. On the other hand, the EPR signal of the irradiated solution of H_2TTP was stable only in the rigid glass and decayed completely on warming above 180 K.

Discussion

Photolysis of these porphyrins and metalloporphyrins has resulted in absorption spectra which are consistent with absorption spectra that are found upon the formation of porphyrin π-cation radicals at room temperature, using chemical [5], electrochemical [23], and photochemical [6] methods. Although the ground state assignment can only be substantiated using MCD [5] and EPR [3] spectra, the absorption spectra do appear to reflect the character of the $^2A_{2u}$ and $^2A_{1u}$ ground states that are possible for the porphyrin π-cation radicals, where for $ZnTPP^{+\bullet}$ the ground state is $^2A_{2u}$ and for $MgOEP^{+\bullet}$ the ground state is $^2A_{1u}$ [3, 5, 24].

The data presented above indicate that light induced oxidation of porphyrins occurs in alkyl chloride solutions containing TCE or CCl_4, as a result of electron transfer from the porphyrin to the solvent acceptor molecules. The photochemical process may be represented as

$$P \xrightarrow{h\nu} P^* \qquad (1)$$

$$P^* \longrightarrow P \qquad (2)$$

$$P^* + RCl \xrightarrow{k_t} P^{+\bullet} + R^\bullet + Cl^- \qquad (3)$$

where P* is a porphyrin in an electronically excited state.

It should be noted that with irradiation of the samples with light of low intensity and low energy, biphotonic ionization, or the involvement of higher energy excited singlet or triplet states are both unlikely processes. The differences between the optical and EPR spectra of the $P^{+\bullet}$ formed in the rigid matrix and in the fluid solution indicate that the distribution of the unpaired electron density over the porphyrin ring is not the same in the reactions that take place in the solid and solution phases. It is unclear at present whether this is an effect of a 'cage' interaction between the spins located on the porphyrin cation and the solvent radical, or is a result of a strained configuration of the oxidized porphyrin ring due to the frozen matrix.

The identification of the excited state involved in the electron transfer requires studies of the electron transfer rate. The formation of the π-cation radical species from the photoexcited porphyrin in the rigid solution, in the absence of a charge-transfer complex between the donor porphyrin and the acceptor solvent molecules, indicates the importance of an electron tunneling mechanism. The ionization potential of tetraphenylporphyrins, which have been measured in the condensed phase, are of the order of 6 eV [25]. Assuming that the lowest triplet state is photoactive in the electron transfer, estimates of the energy required to remove an electron from the excited porphyrin, and place it in the solvent, yield the value of about 4.5 eV (*cf.* Table I). At this binding energy for the electron donor, quantum mechanical theories [26–28] suggest that the transfer of electrons will still occur at a reasonable rate.

In frozen glassy solutions the donor–acceptor distances are fixed and can be considered as randomly distributed. The relationship between the survival probability P or P* in the above equations and the tunneling distance R could be assumed to have the same form as for other long range electron transfer reactions with no diffusion involved [29, 30]:

$$\mathbf{P} = \exp(-4/3\ \pi R^3 c)$$

where c is the acceptor concentration.

The efficiency of electron transfer in the overall photochemical process is proportional to the product

$$(1 - \mathbf{P3})\mathbf{P2},$$

where **P2** and **P3** are the probabilities that P* has not decayed by either processes 2 or 3, respectively. This would give the following dependence of the yield of $P^{+\bullet}$ on the concentration of the acceptor:

$$\phi \propto (1 - \exp(-4/3\pi R^3 c))$$

The dependence of the electron transfer efficiency on the excited state lifetime, as related to **P2**, could partially explain the observed differences in the yield of $P^{+\bullet}$, ϕ, among the porphyrins (*cf.* Table I) if the lowest triplet state was to be involved.

However, a general explanation for the electron transfer efficiency resides in the value of the rate constant, k_t, which can be related both to the electron transfer distance and to factors such as reaction exothermicity, temperature, and molecular rearrangements [30, 31].

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